

$\text{Ru}_2\text{Ge}_3$ : CRYSTAL GROWTH AND SOME PROPERTIES

Alex Borshchevsky and Jean-Pierre Fleurial  
 Jet Propulsion Laboratory/ California Institute of Technology  
 Pasadena, CA 91109

Abstract

Large samples of  $\text{Ru}_2\text{Ge}_3$  were grown from Ge-rich off-stoichiometric melts at a temperature close to  $1460^\circ\text{C}$  by a vertical gradient freeze method in graphite and glassy carbon crucibles. Diffusionless transition from high temperature tetragonal structure to low temperature orthorhombic structure causes twinning and crack formation. Thermal expansion coefficients of both low and high temperature phases were measured. Some electrical transport properties in the 25-  $1000^\circ\text{C}$  temperature range in different crystallographic directions are also described for this high temperature semiconductor. Substantial anisotropy is observed.

1. Introduction

Ruthenium sesquigermanide,  $\text{Ru}_2\text{Ge}_3$ , and its isostructural analogues  $\text{Ru}_2\text{Si}_3$ ,  $\text{Ru}_2\text{Sn}_3$ ,  $\text{Os}_2\text{Si}_3$  and  $\text{Os}_2\text{Ge}_3$  are known as "chimney-ladder" compounds characterized by long tetragonal unit cells consisting of  $\beta$ -tin subcells of transition elements stacked one on top of the other, and a helical arrangement of the other elements [1]. They have been shown to undergo a diffusionless phase transformation from an orthorhombic centro-symmetric low temperature structure to a tetragonal non-centrosymmetric high temperature structure [2]. These transformations, due to short displacements of the Si, Ge or Sn atoms, are reversible and occur gradually over a wide temperature range. Some properties of the  $\text{Ru}_2\text{Si}_3$  and  $\text{Ru}_2\text{Ge}_3$  compounds were previously investigated by preparing several resmeltings of Ru and Ge(Si) in RF and arc furnaces until the final products contained only single phase defined by metallography and X-ray powder diffraction analysis [2,3]. Both materials demonstrated semiconducting properties with high temperature modifications energy gaps of 0.44 and 0.34 eV, respectively. These gaps increase discontinuously while the compounds undergo diffusionless phase transformations into the low temperature modifications.

We decided to investigate  $\text{Ru}_2\text{Ge}_3$  in particular because of its high melting point, complex crystal structure and high density which could possibly result in attractive high temperature semiconducting properties. The purpose of the present study was to use crystal growth to obtain

much larger samples and characterize the material.

The original Ru-Ge phase diagram can be found in [4] and fig. 1 represents the more recently assessed diagram redrawn from [5]. While the monogermanide RuGe is a congruently melting line compound, Ru<sub>2</sub>Ge<sub>3</sub> decomposes peritectically at a temperature of 1470°C. Growth from the melt of Ru<sub>2</sub>Ge<sub>3</sub> can be achieved next to this temperature by crystallization of slightly off-stoichiometric Ge-rich solutions (see an arrow in the insert, for example). However, the published data did not precise the composition for the end of the peritectic plateau.

## 2. Experimental details

### 2.1. Synthesis and crystal growth.

Stoichiometric and Ge-rich samples weighing 2g were synthesized in graphite crucibles with lids under Ar flow using an induction furnace. The temperature was controlled by an optical pyrometer within  $\pm 5^\circ\text{C}$ . After 30 minutes at 1500°C, the melts were quickly cooled down by shutting off the furnace power. Characterization of the resulting samples was conducted by microprobe analysis (MPA) and room temperature Hall effect measurements (Van der Pauw method),

Crystal growth of large ingots was performed in CVD graphite (Union Carbide) and glassy carbon (Sign Corp.) crucibles of 12mm ID and 80mm high with a conical bottom. During the processing, the crucibles were covered by lids to minimize evaporation of Ge and other volatile components. The water-cooled, aluminum furnace chamber (the furnace was manufactured by Thermal Technology, Inc., Astro div.) accommodated two cylindrical graphite resistance heating elements, vertically oriented. Temperatures of both elements were independently controlled within  $\pm 2^\circ\text{C}$  through the sight windows by two optical pyrometers with controllers/programmers. The temperature gradients were measured by two thermocouples, Pt-PtRh and WRe. During the calibration runs as well as during the growth, the chamber was purged with high purity helium,

The loads were placed into the crucible, covered by the lid and installed into the furnace so that the tip of the crucible was located at the lower part of the  $50^\circ\text{C}/\text{cm}$  temperature gradient. Simultaneous lowering of the temperatures of both zones provided an uniform translation of the solid-liquid interface from the bottom of the crucible, furnace assembly and crucible remaining stationary. Typical crystal growth rates of about 10 mm/day were used.

### 2.2. Metallography and microprobe analysis

Suitable samples were cut using a diamond saw, mounted in epoxy, ground and polished. The microstructure were investigated by microscopic examination using an optical Nikon metallurgical microscope with and without light polarization or Nomarski contrast. An etching solution of 1.2g K<sub>3</sub>Fe(CN)<sub>6</sub>, 0.8g KOH and 10ml of water was used at room temperature for 1-3

min to reveal the microstructure of some of the samples.

MPA was performed on a JEOL JXA-733 superprobe (electron microprobe) operating at a 20kV acceleration potential and a 25x10-9A probe current. Standards used initially were Ge and Ru metals of highest possible purity and later on a single crystalline sample of  $\text{Ru}_2\text{Ge}_3$  compound. Pure elements were used as standards to analyze their concentrations when added to  $\text{Ru}_2\text{Ge}_3$  as dopants. X-ray intensity measurements of peak and background were made using wavelength dispersive spectrometry (WDS) and intensities were converted to concentrations units with the Armstrong-CITZAF software package used at California Institute of Technology.

The density of the samples was measured by the immersion technique. The samples were precleaned in methanol, placed in a platinum basket and weighed in air and in pure toluene, taking into account ambient temperature.

### 2.3. X-ray investigations.

X-ray techniques were used to check the single crystallinity of the samples and their crystallographic orientation (1.sue) and to estimate the thermal expansion coefficient temperature dependence in as wide a temperature range as possible (high temperature diffractometry). Laue pictures were taken on several different sections of ingots using molybdenum and copper radiation at 28kV, 18 mA, with a specimen-to-film distance of about 3 cm. A Siemens D-500 diffractometer equipped with a vacuum hot stage was used to measure the change in lattice parameter with temperature for the powdered ruthenium germanide samples in agate mortar. The incident X-ray was  $\text{Cu K}\alpha$  and the detector was a NaI scintillator with a graphite monochromator. The powder was distributed on the platinum stage and a scan was taken at room temperature. The samples were heated at 10°C intervals up to 700°C and then allowed to cool at 20°C/min. During cooling, X-ray scans were taken at 600, 300°C and room temperature. The platinum diffraction was recorded at each temperature interval for calibration purposes. Above 700°C the maxima, even of the most intensive lines, were so diffused that their positions and corresponding d-spacing calculations became too difficult to estimate.

### 2.4. Transport properties

One large single crystalline sample of cylindrical form (3.5 mm thick) was used for speed of sound measurement along the growth direction at room temperature.

Small 1 mm thick samples were also prepared and measured at room temperature for Hall effect and electrical resistivity by the van der Pauw method. Some samples were measured from room temperature up to 1000°C using a specially designed sample holder [6]. Because of the long and narrow "chimney ladder" structure of  $\text{Ru}_2\text{Ge}_3$ , anisotropy of the transport properties was expected from measurements along different crystalline orientations. From one of the ingots, two slices were cut, one with faces parallel to growth direction, [ 11 ()], and one with faces

perpendicular to it ( $[\bar{1}\bar{1}\bar{1}]$ , see Fig.3).

### 3. Results and discussion.

#### 3.1. Microstructure and preferential growth direction,

First growth experiments with various Ru and Ge compositions showed that good quality single phase  $\text{Ru}_2\text{Ge}_3$  samples could be obtained from melts 38 at.% Ru and 62 at.% Ge. Compositions closer to the 2:3 stoichiometric ratio resulted in inclusions of  $\text{RuGe}$ , thus demonstrating that the peritectic plateau of  $\text{Ru}_2\text{Ge}_3$  extended to 38:62 ratio. A typical directionally crystallized ingot of  $\text{Ru}_2\text{Ge}_3$  is shown in fig.2. Most of the ingots were single phase, the extra Ge material lying at the very top because of the liquid-solid interface translation during crystallization from the bottom up. Polycrystalline ingots, even with grain cross-sections of 5-7mm, were heavily cracked. However, most of the cracks were located at the grain boundaries, thus the trackless single crystalline grains with dimensions of up to 6x6x3 mm<sup>3</sup> were readily available for investigation. Only completely single crystalline ingots were found to be crack-free. Polished and etched, single crystals revealed fine lines continuing in the same direction (Fig.3). These lines are not fine inclusions as originally thought, but are etched shallow grooves that is not a compositional but a topographical feature. It has been proven, by a thorough MPA investigation, that the material at the bottom of the groove corresponds to the 2:3 compound. It was also shown that the width and the depth of the grooves depend on the time of etching. It was found earlier that  $\text{Ru}_2\text{Ge}_3$  undergoes diffusionless phase transformation with temperature [2,3]. The high temperature tetragonal modification (space group  $P4c2$ ) transforms into low temperature orthorhombic structure with space group  $Pbcn$  through another orthorhombic structure,  $Pb2n$ . The transformation is reversible and occurs gradually over a wide temperature interval (within approximately 400-600°C). It is clear that the growth of the crystal starts from high temperature tetragonal modification and only at much lower temperatures does the tetragonal structure gradually transform into orthorhombic (Fig.4) by a small displacement of Ge atoms [2,3]. During this transformation, dimension "a" practically doubles while "b" and "c" remain the same. Thus, within 400-600°C temperature interval a displacive transformation involving a distortion of the structure, reduces the symmetry from tetragonal to orthorhombic. This transformation is very rapid and the high temperature modification cannot be retained even during fast cooling (one of the samples was sealed into quartz ampoule, annealed at 800°C for 24 hrs and quenched into water and resulted in low temperature modification). Obviously, the transformation involves a change of the shape of the unit cell and lattice parameters. Local strains occur resulting in twinning. We consider that the lines shown on Fig.3 are twins releasing the strains. Sometimes even further release of strains occurs with developing of needle twins (Fig.5) or even cracking of single crystal (Fig.6). It can be seen that twin boundaries continue across the microcracks, in the same directions, only slightly shifted along

the cracks, as a result of displacement. This type of phenomenon has been described in the literature and recently summarized in [7] using mineral leucite ( $\text{KAlSi}_2\text{O}_6$ ) as an example.

To check the single crystallinity of one of the crack-free ingots, two Laue pictures were taken of two different spots on the vertical cut of the ingot. The two photos showed identical crystal orientation at both locations despite the fact that their positions were far away from each other. The Laue pattern of this surface corresponded to [11 0] standard stereographic projection for orthorhombic space group *pmcn* indicating that this direction is a preferential growth direction for this compound when grown from the melt without any seeding (Fig.4).

### 3.2. Thermal expansion, crack formation and density.

During the experiments, it was found that crack formation often occurs when the material crystallizes from a near-stoichiometric melt. The thermal expansion coefficient vs. temperature measurements were undertaken to verify that the phase transformation and/or anisotropy can cause this undesirable phenomenon. The results of these measurements are shown in fig.7. Indeed, the thermal expansion coefficients are quite different for the two phases. In approximately the middle of the transformation interval, which is about 400-600°C, the coefficients in direction “a” are  $7.10 \times 10^{-6}$  and  $10 \times 10^{-6}/\text{deg}$  for tetragonal and orthorhombic phases, respectively. This difference, during the cooling, might result in stresses causing the cracks formation. It is clear, from figure 7, that the thermal expansion coefficients are negative which means that cooling causes an ‘expansion’ of the material,

Presently, single crystalline ingots of the material revealed minimal crack formation. The experimental densities of such ingots were found to be  $9.17 \text{ g/cm}^3$  which is more than 98% of the theoretical value of  $9.23 \text{ g/cm}^3$ .

### 3.3. Transport properties

The speed of sound measured along the growth direction of a large single crystal of  $\text{Ru}_2\text{Ge}_3$  resulted in a value of  $5737 \pm 170 \text{ m/s}$  at room temperature. A corresponding Debye temperature  $\theta_D$  of 346K was calculated, to be compared with a value of 435K determined from low temperature specific heat measurement [3].

All samples of  $\text{Ru}_2\text{Ge}_3$  grown from a slightly Ge-rich melt obtained in this effort were of P-type conductivity in contrast to the n-type conductivity of samples prepared by arc melting and subsequent annealings [3]. Results from high temperature Hall effect and electrical resistivity measurements performed on two single crystalline samples cut from the same ingot and of orientation perpendicular to each other are reported on figures 8 and 9. The effect on the transport properties of the transition from the low temperature orthorhombic structure to the high temperature

tetragonal structure can be clearly observed on both figures. There is a hysteresis effect since during the course of the measurements the transition would occur at about 550°C when heating samples up to 1000°C and about 450°C when cooling samples down to room temperature.

Based on analysis of the variation of  $\ln(p)$  as a function of  $1/T$  (figure 8) when approaching the intrinsic regime, values for the band gap of the low temperature and high temperature structural phases were evaluated as 0.69 eV and 0.57 eV respectively. These results are to be compared with values of 0.52 eV and 0.34 eV obtained by Susz [3]. Values obtained for the low temperature phase are to be taken as 'lower limits for the band gap because no true intrinsic behavior could be achieved before the structural transition to the high temperature phase took place. A separate photoelectrochemical measurement carried out on a thin slice of single crystalline material estimated the room temperature band gap to be 0.87 eV, a value substantially larger than the one obtained from the high temperature electrical resistivity variations.

Figures 8 and 9 also showed that large anisotropic ratios exist for electrical resistivity and Hall coefficient measured parallel and perpendicular to the growth direction. Hall coefficient and electrical resistivity values along the growth direction ([110] orientation) were more than one order of magnitude larger in this particular sample.

### Conclusions

1. Ru<sub>2</sub>Ge<sub>3</sub> crystals were grown from slightly off-stoichiometric melt by gradient-freeze technique.
2. The preferential direction of growth was found to be [110].
3. The phase transition during cooling causes twinning and sometimes even crack formation.
4. Substantial difference in thermal expansion coefficients for low and high temperature modifications was measured. This is another possible reason for crack formation.
5. High temperature Hall effect and electrical resistivity showed semiconducting behavior with strong anisotropy of transport properties measured parallel and perpendicular to growth direction.

### References

1. D.J. Poucharovsky and E. Parthe, "The Orthorhombic crystal structure of Ru<sub>2</sub>Si<sub>3</sub>, Os<sub>2</sub>Si<sub>3</sub> and Os<sub>2</sub>Ge<sub>3</sub>", *Acta Cryst.*, B30, 2692 (1974).
2. D.J. Poucharovsky, K. Yvon and E. Parthe, "Diffusionless phase transformations of Ru<sub>2</sub>Si<sub>3</sub>, Ru<sub>2</sub>Ge<sub>3</sub> and Ru<sub>2</sub>Sn<sub>3</sub>. I. Crystal structure investigations", *J. Less Common Metals*, 40, 139 (1975).
3. C.P. Susz, J. Muller, K. Yvon and E. Parthe, "Diffusionless phase transformations of Ru<sub>2</sub>Si<sub>3</sub>, Ru<sub>2</sub>Ge<sub>3</sub> and Ru<sub>2</sub>Sn<sub>3</sub>. II. Electrical and Magnetic Properties", *J. Less Common Metals*,

71,P1(1980).

4.E. Raub and W. Fritzsche, "Germanium-Ruthenium Legierungen", Z. Metallk. 53,779 (1963).

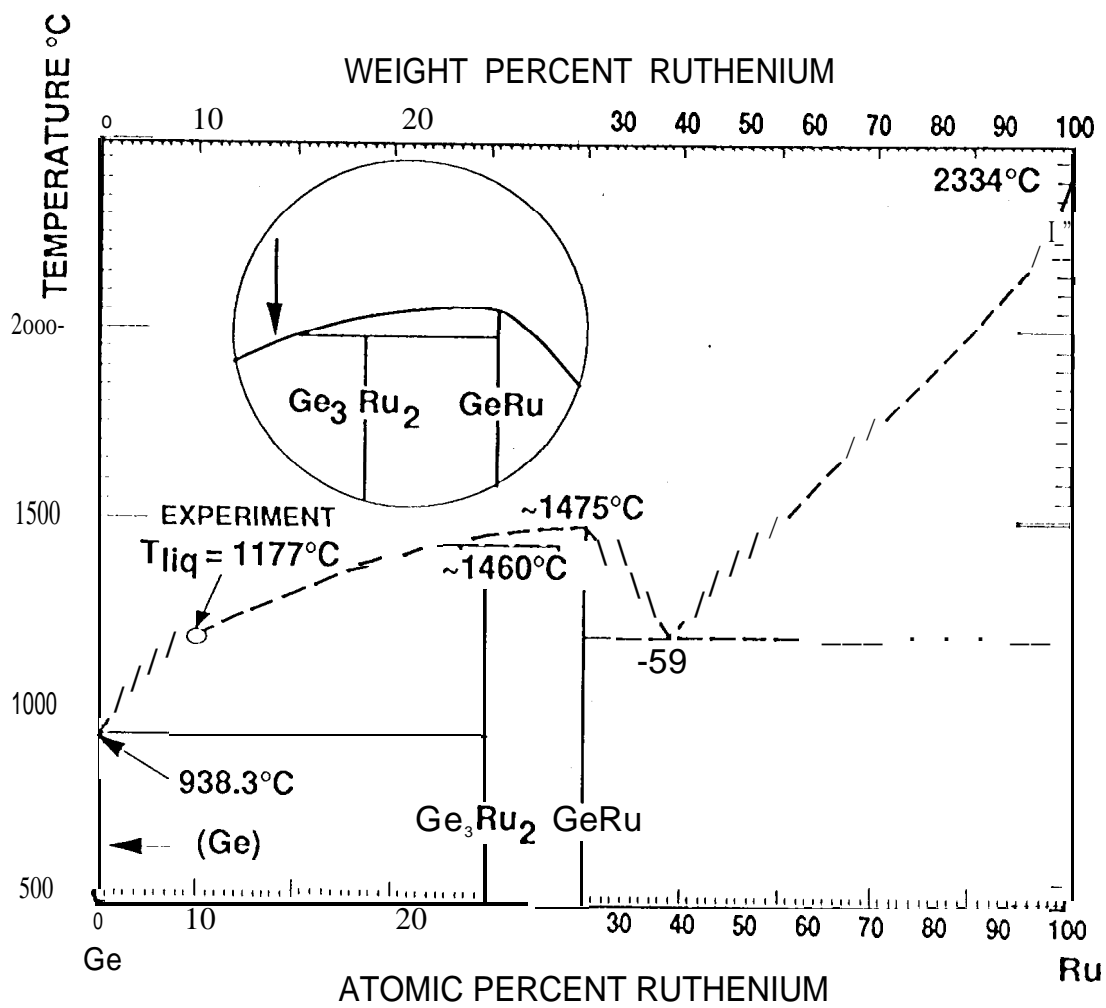
5. Binary Alloy Phase Diagrams, 2nd ed., Ed, T. B. Massalski, ASM Int., 1990, p.1992.

6.J. McCormack and J.-P. Fleurial, 'Electrical Measurements of SiGe Thin Films', in Modern Perspectives on Thermoelectrics and Related Materials, MRS Symp. Proc. Vol. 234, p. 135, Materials Research Society, Pittsburg, Pennsylvania, (1991).

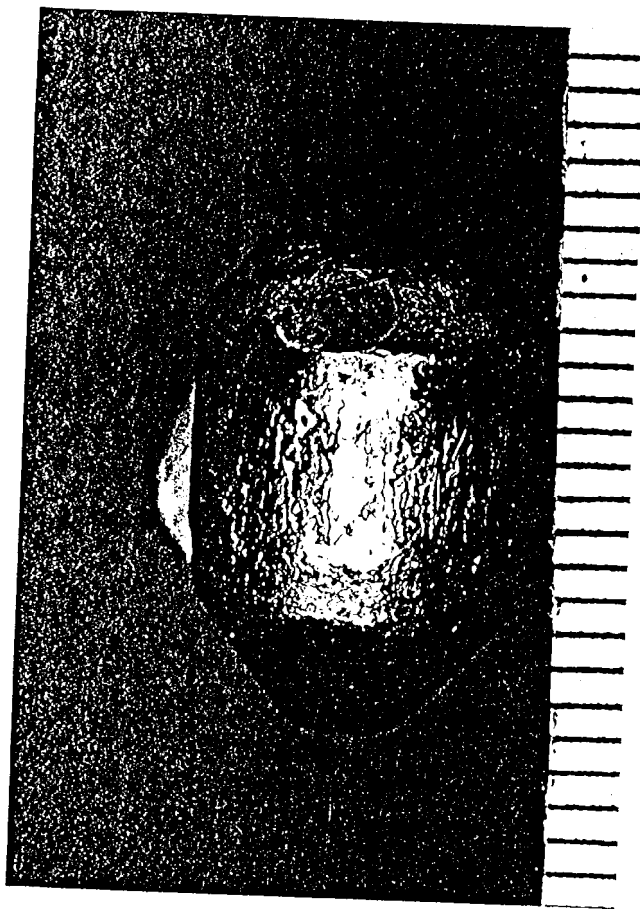
7, A. Putnis, "Introduction to Mineral Sciences", Cambridge, University Press, 1992, p.223.

#### Acknowledgments

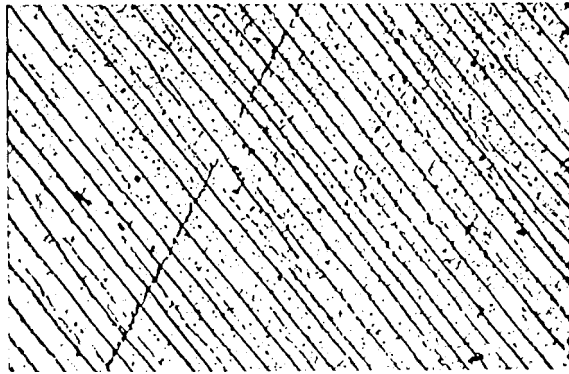
The work described in this paper was carried out at the Jet Propulsion Laboratory/California Institute of Technology, under the contract with National Aeronautics and Space Administration. This work was sponsored by the Knolls Atomic Power Laboratory, Schenectady, New York. The authors would like to thank Denise Irvine for samples preparation, Jim Kulleck and Lynn Lowry for x-ray examination, Paul Carpenter for microprobe analysis and Amy Ryan for photoelectrochemical measurements.







~~in-dop~tingot, stoichiometric,  
Bridgman/Gradient Freeze grown in  
glassy carbon crucible~~



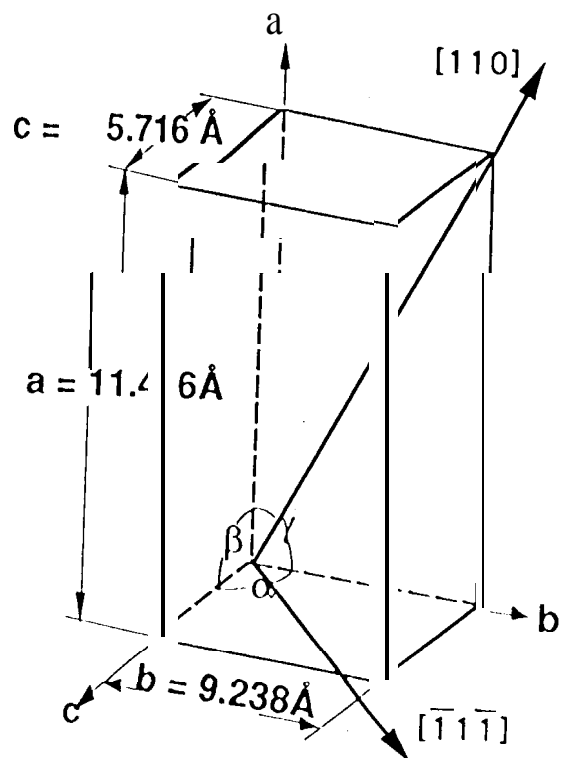
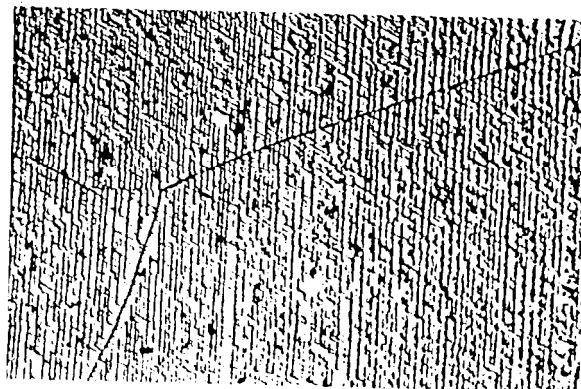
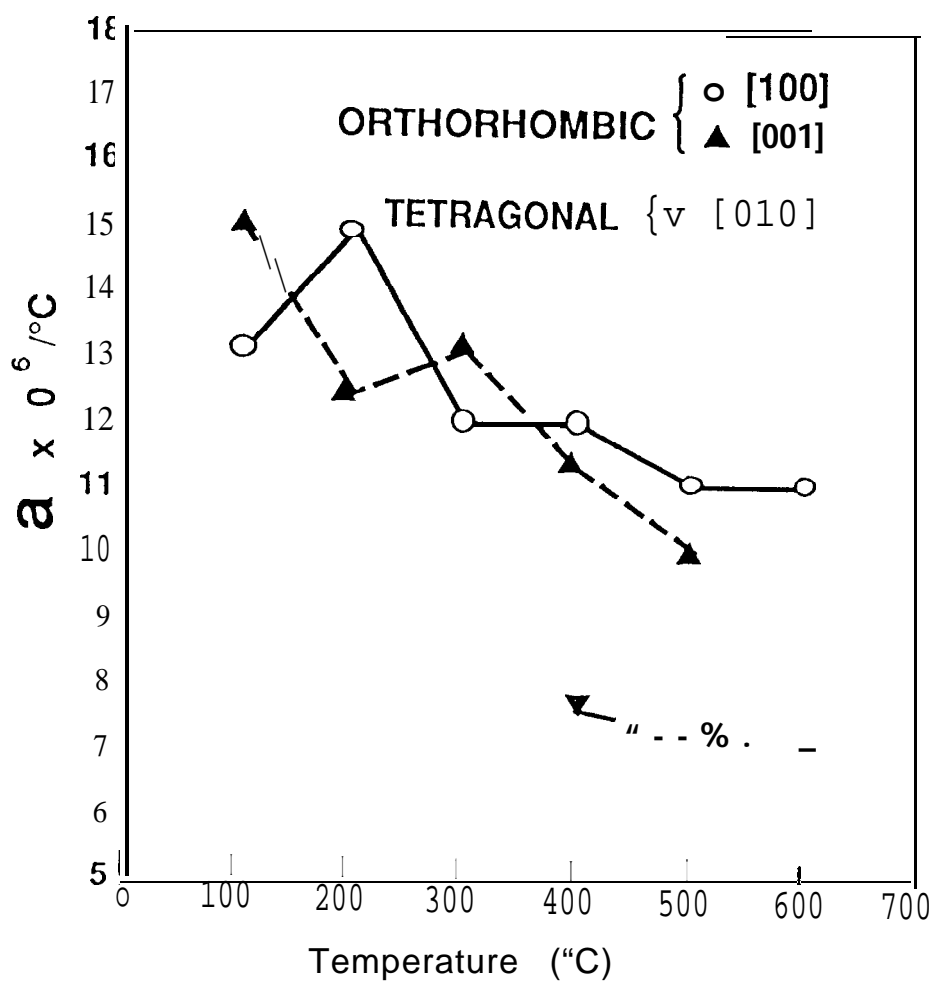
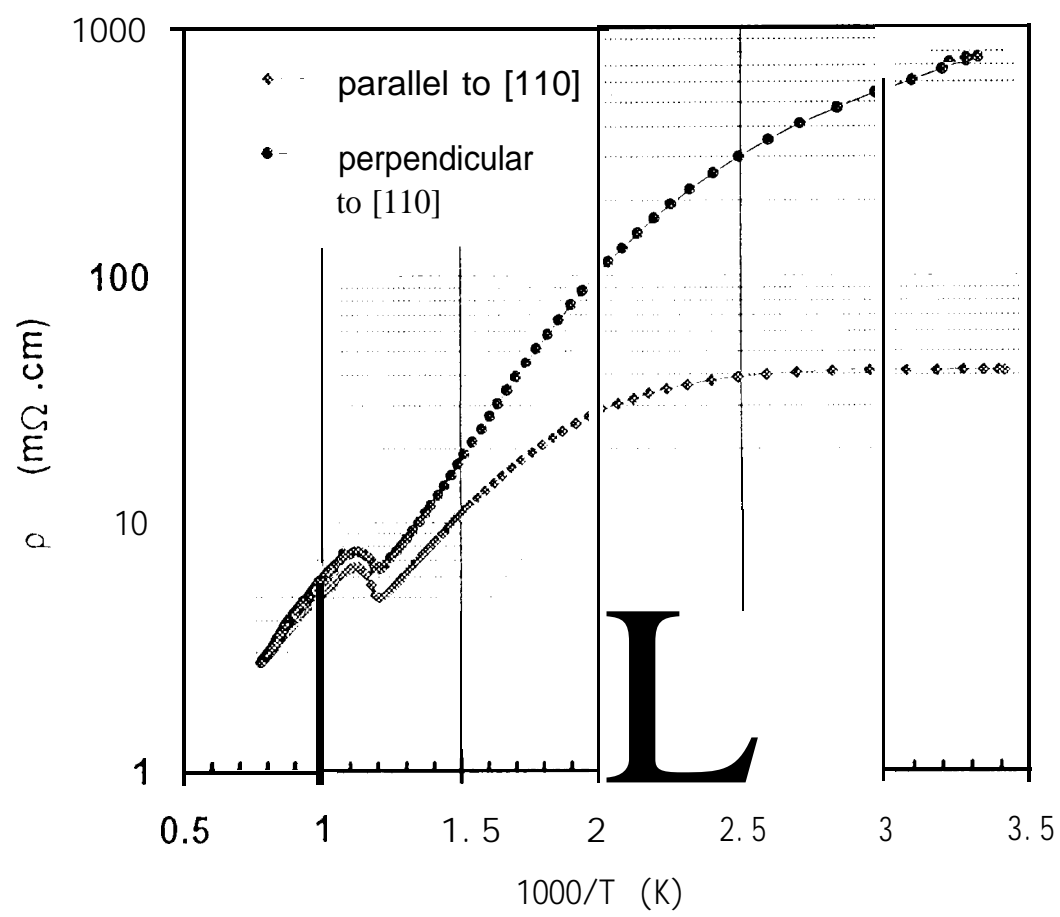


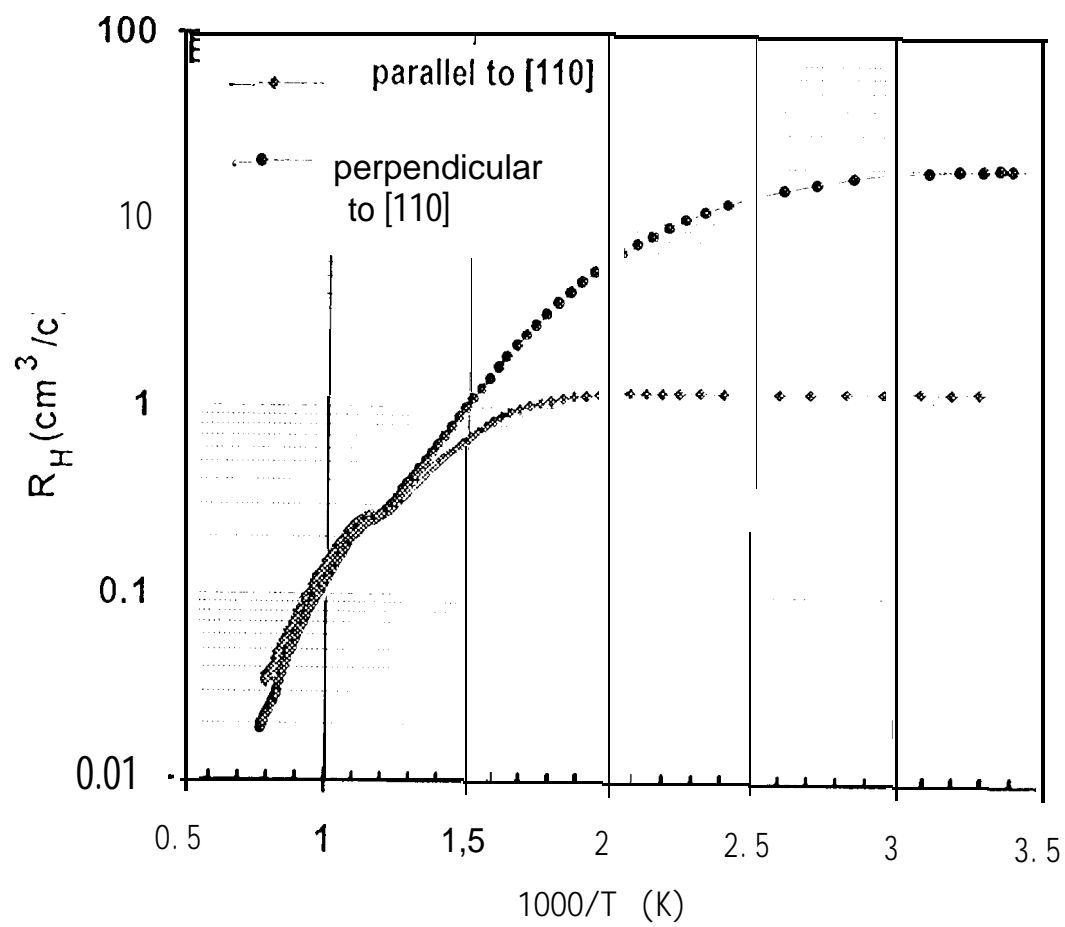


Fig. 5











A, Borshchevsky, J-P-Fleurial

"Ru<sub>2</sub>Ge<sub>3</sub>: crystal growth and some properties", A 26

#### Figure captions

Fig 1. Ru-Ge phase diagram,

Fig 2. Ru<sub>2</sub>Ge<sub>3</sub> ingot,

Fig 3. Twins on single crystal, polished and etched, x400.

Fig 4. Unit cell of low temperature orthorhombic modification. [11 0] is a preferential growth direction and  $[\bar{1}\bar{1}\bar{1}]$  is approximately perpendicular to it.

Fig.5. Needle twins on single crystal, annealed above transition point, quenched, then annealed below transition point, polished, etched, x50.

Fig.6. Twins and cracks on single crystal, polished, etched. x200.

Fig.7. Linear expansion coefficients for high and low temperature modifications.

Fig.8. High temperature electrical resistivity of single crystal measured parallel and perpendicular to the growth direction, [1 10].

Fig.9. High temperature Hall coefficient.